ELSEVIER

Talanta 43 (1996) 77–87

Talanta

Determination of traces of chromium in cocaine and heroin by flameless atomic absorption spectrometry

Pilar Bermejo-Barrera*, Antonio Moreda-Piñeiro, Jorge Moreda-Piñeiro, Adela Bermejo-Barrera

Department of Analytical Chemistry, Nutrition and Bromatology, Faculty of Chemistry, University of Santiago de Compostela, 15706-Santiago de Compostela (A Coruña), Spain

Received 21 February 1995; accepted 14 August 1995

Abstract

A method for the determination of total chromium in cocaine and heroin by flameless atomic absorption spectrometry is presented. Cocaine samples were dissolved in 2 ml of HNO_3 35.0% (v/v) and diluted to 10 ml with ultrapure water; heroin samples were dissolved in ultrapure water, adding 0.4 ml of HNO_3 35.0% (v/v) to dissolve inert species, and also diluted to 10 ml. $Mg(NO_3)_2$ and HNO_3, as chemical modifiers, were compared in terms of sensitivity, precision and accuracy, a lower detection limit being obtained for the use of $Mg(NO_3)_2$, 5.77 $\mu g\ kg^{-1}$ (7.23 $\mu g\ kg^{-1}$ for HNO_3). Within-batch precision was found to be 6.19% and 1.48% for drug solution spiked with 0 and 10 $\mu g\ l^{-1}$ of Cr^{3+}, respectively, when using $Mg(NO_3)_2$, and 7.45 and 1.19% for the same respective concentration levels when using HNO_3. Similar results on analytical recovery were obtained for both $Mg(NO_3)_2$ and HNO_3. $Mg(NO_3)_2$ was selected as the more adequate of the two chemical modifiers. A study of the introduction of a cooling-down step of 50°C was carried out and compared in terms of sensitivity to the programme without a cooling-down step, but no advantage was observed. Studies on the variation in precision and analytical recovery with the amount of sample, and interferent effects of different species on chromium determination were developed. Finally, chromium concentrations obtained in cocaine samples varied between 0.02 and 0.14 mg kg^{-1}, the levels in the heroin samples being in the 0.05–0.59 mg kg^{-1} range.

Keywords: Chromium; Cocaine; Heroin; Chemical modifiers; Magnesium nitrate modifier; Flameless absorption spectrometry

1. Introduction

The remarkable increase in the improper use of cocaine and heroin, two of the more dangerous narcotics, has led to the imposition by the International Community of a control on the trade and utilization of these drugs. Therefore, it is very important to determine whether a confiscated drug comes from a certain geographical area. In this way, it is possible to discover its trading routes. Such studies are usually based on organic

*Corresponding author.

SSDI 0039-9140(95)01718-6

compounds present in drugs, and thus extensive information is available on the organic constituents in cocaine and heroin. However, knowledge about the inorganic constituents of these substances is very poor. In this sense, only few data have been found in the literature on metallic species [1], chromium being one of the metals whose presence has been reported. According to the chromium concentration found [1], it can be concluded that it is a trace constituent in cocaine, being present in levels between 0.2 and 1.6 mg kg^{-1}. The concentration interval reported for heroin [1] is 0.2–140 mg kg^{-1}. The chromium concentration in a great number of samples cannot be determined easily by inductively coupled plasma-atomic emission spectrometry, which is the technique employed by Violante et al. [1] in their studies, because it is lower than the detection limit of the technique.

Flameless atomic absorption spectrometry (FAAS) has been recognized as one of the best techniques for determining metal content, chromium being one of the metallic species requiring very sensitive detection [2].

As there is no literature on the determination of chromium in samples such as cocaine and heroin, in order to select the most adequate chemical modifier, a bibliographic search was carried out on the determination of chromium in biological and environmental materials and waters [3–28]. It should be mentioned that as a consequence of the refractory behaviour of chromium [2,29], it has been proposed not to add a chemical modifier [3–5]. However, it is evident that the low charring temperatures obtained in the absence of a matrix modifier do not offer satisfactory matrix volatilization when the samples contain complex matrices; thus, the addition of a chemical modifier appears to be necessary. The use of nitric acid [6–8] as a chemical modifier was therefore proposed, charring occurring at 1300°C. The addition of Na_2WO_4, in solution [7–9] or the use of W-coated graphite tubes [10,11], has also been reported; the former was of more advantage, owing to the large difference in charring temperatures reported, i.e. 1600°C for addition in solution and 900°C for the use of coated graphite tubes. The use of graphite tubes coated with Zr [9], Ta [11,12] and La [13,14] has also been reported. Vanadium and molybdenum [15] have been proposed for chromium determination, achieving a charring temperature of 1400°C. Finally, NH_3 [16] and ascorbic acid [17] have also been used as chemical modifiers for chromium.

Magnesium nitrate alone [7,9,18–24], or in conjuction with palladium [25] or calcium [26,27], appears to be the most adequate chemical modifier for chromium, owing to the higher charring temperatures reported. In this sense, palladium has also been proposed as an adequate chemical modifier [14,28]. In addition, these species present the advantage, in comparison with the other chemical modifiers cited, that their content is not frequently determined by FAAS; hence, their use in large amounts, mg l^{-1}, as chemical modifiers does not lead to contamination of the graphite furnace.

In this paper, the use of nitric acid and magnesium nitrate as chemical modifiers for chromium determination is compared, investigating also palladium and the mixture palladium–magnesium nitrate proposed by Welz et al. [30]. Finally, a method for chromium determination in cocaine and heroin was developed and applied to different samples.

2. Experimental

2.1. Apparatus

AAS measurements were performed with a Perkin-Elmer model 1100B atomic absorption spectrometer equipped with an HGA 700 graphite furnace, an AS-70 autosampler and a deuterium arc background corrector. A Cr hollow cathode lamp (Perkin-Elmer) operated at 25 mA, which provided a 357.9 nm resonance line, was used. The spectral bandwidth was 0.7 nm. Pyrolytically graphite-coated graphite tubes and L'vov graphite platforms were used throughout.

2.2. Reagents

All the solutions were prepared from analytical-reagent grade chemicals using ultrapure water,

resistivity 18 MΩ cm^{-1}, which was obtained by means of a Milli-Q (Millipore, USA) water purification system.

Nitric acid stock standard solution, 35.0% (v/v), was prepared from nitric acid Aristar, 69.0–70.5% (v/v) (BDH Chemicals, Poole, UK) with a maximum chromium content of 0.05 mg l^{-1}.

Chromium nitrate stock standard solution, 1.000 g l^{-1}, was obtained from Merck (Darmstadt, Germany).

Magnesium nitrate stock standard solution, 2.000 g l^{-1}, was prepared by dissolving 2 g of magnesium nitrate (Analar, BDH Chemicals) in 1 l of ultrapure water.

Palladium stock standard solution, 3.000 g l^{-1}, was prepared according to Welz et al. [31] by dissolving 300 mg of palladium (99.999%, Aldrich, Milwaukee, WI, USA) in 1 ml of concentrated nitric acid and diluting to 100 ml with ultrapure water. If the dissolution was incomplete, 10 μl of hydrochloric acid (Aristar, 35.0% (v/v), BDH Chemicals, with a maximum chromium content of 0.005 mg l^{-1}) was added to the cold nitric acid and heated to gentle boiling in order to volatilize the excess chloride.

2.3. Procedure

Cocaine samples, 0.5 g, were dissolved in 2 ml of nitric acid 35.0% (v/v), diluting to 10 ml with ultrapure water. For heroin samples, 0.25 g of sample was dissolved in ultrapure water, and 0.4 ml of nitric acid 35.0% (v/v) was added to dissolve any remaining undissolved inert substances. The solutions were then diluted to 10 ml with ultrapure water. All samples were kept in polyethylene vials at 4°C.

0.5 or 0.25 ml of cocaine and heroin solution, respectively, was transferred to an autosampler cup, adding an adequate volume of magnesium nitrate to obtain a concentration of 15 mg l^{-1} after dilution to 1 ml. Calibration was performed over the 0–10 μg l^{-1} range, injecting 20 μl into the atomizer, and running the sequential dry–charring–atomization–cleaning programme of the graphite furnace shown in Table 1.

3. Results and discussion

3.1. Comparative study of palladium, magnesium nitrate, palladium–magnesium nitrate and nitric acid as chemical modifiers

A comparative study on the use of palladium, magnesium nitrate, palladium–magnesium nitrate and nitric acid as chemical modifiers for the determination of chromium in cocaine and heroin was developed. Charring curves corresponding to each chemical modifier were obtained for a cocaine sample solution spiked with 10 μg l^{-1} of Cr^{3+}, for a heroin sample solution and for an aqueous standard solution of 15 μg l^{-1} of Cr^{3+}, Figs. 1(a), 1(b) and 1(c), respectively. The atomization temperature used was 2500 °C (Table 1) and the concentration of the chemical modifier in these experiments was 10 mg l^{-1} of palladium and magnesium nitrate, and 3.5% (v/v) of nitric acid, i.e. the concentration of nitric acid obtained after dissolution and dilution of the cocaine in the autosampler cups, according to Section 2.3. As can be seen in Figs. 1(a)–1(c), the optimum charring temperatures ranged between 1500 and 1700°C for the different chemical modifiers and solutions. A lower charring temperature, 1500°C, was found for heroin solutions than for cocaine and aqueous standard solutions, 1600 °C, when using palladium–magnesium nitrate. Therefore,

Table 1
Graphite furnace temperature programmes and spectrometer operating conditions[a]. Values in brackets correspond to the use of nitric acid as a chemical modifier

Stage	Temperature (°C)	Ramp (s)	Hold (s)	Ar flow (ml min^{-1})
Drying	150	15	15	300
Charring	1600	10	15 (20)	300
Atomization	2500	0	4	0 read
Cleaning	2600	2	3	300

[a]Cr hollow cathode lamp operating at 25 mA; wavelength 357.9 nm; spectral bandwidth 0.7 nm; integration time 4s; peak-area measurements; injection volume 20 μl; pyrolytic graphite tubes and L'vov platforms.

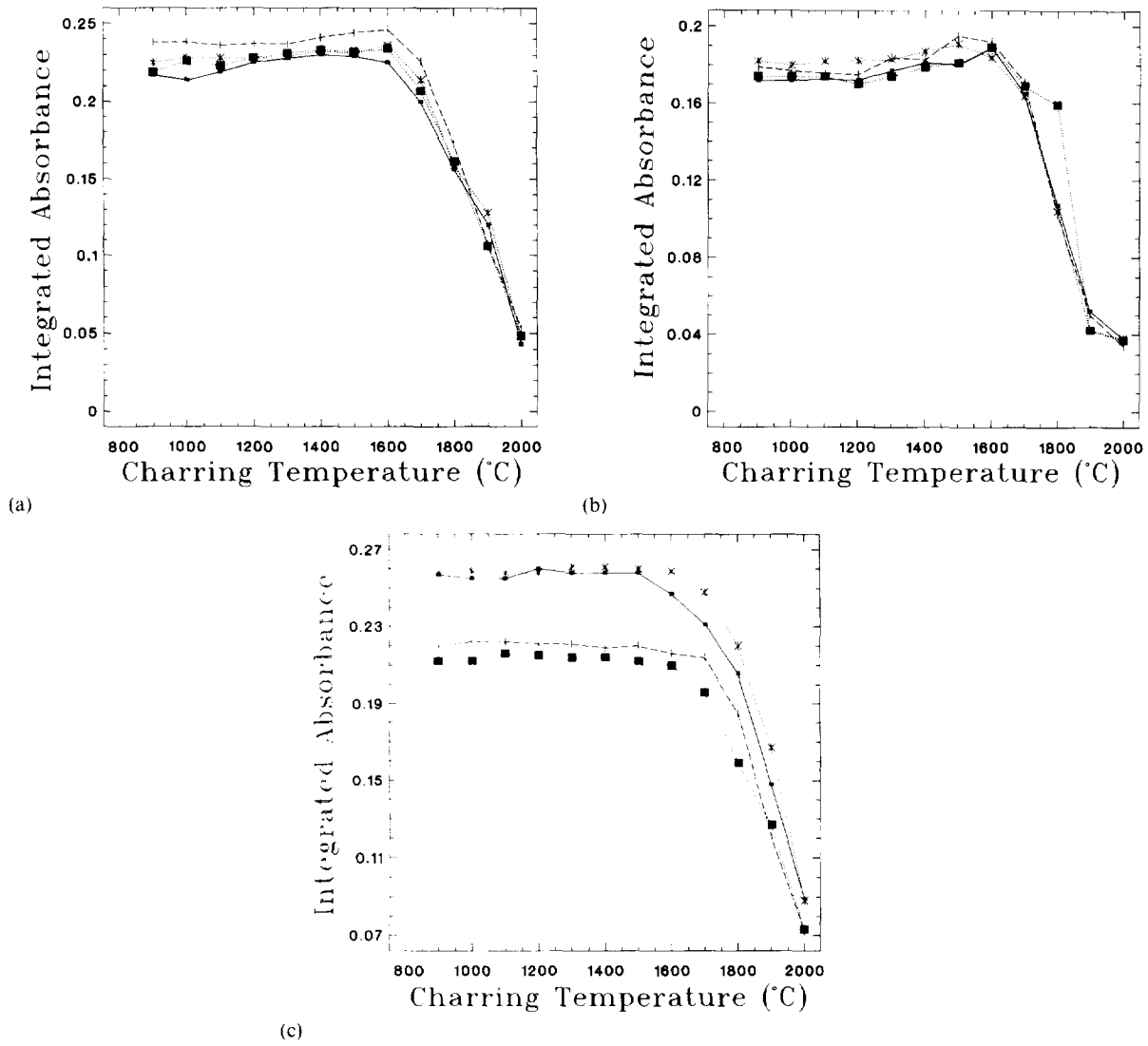

Fig. 1. Charring curves corresponding to (a) cocaine sample solution spiked with 10 $\mu g\ l^{-1}$ of Cr^{3+}, (b) heroin sample solution and (c) aqueous standard solution of 15 $\mu g\ l^{-1}$ of Cr^{3+}, obtained for 10 mg l^{-1} of palladium (■), 10 mg l^{-1} of palladium and magnesium nitrate (*), 10 mg l^{-1} of magnesium nitrate (|) and 3.5% (v/v) of nitric acid (■).

for the use of this chemical modifier, an optimum charring temperature of 1500°C was selected. Similarly, the charring temperature observed for the aqueous standard of Cr^{3+}, 1500 °C, was selected as optimum for palladium. Finally, an optimum charring temperature of 1600°C was chosen when using magnesium nitrate and nitric acid.

Because chromium levels are lower for cocaine than for heroin samples, and hence a greater amount of cocaine is required to prepare the solutions, the following studies were performed on cocaine solutions, considering the results obtained for cocaine solutions are applicable to heroin sample solutions owing to their greater dilution.

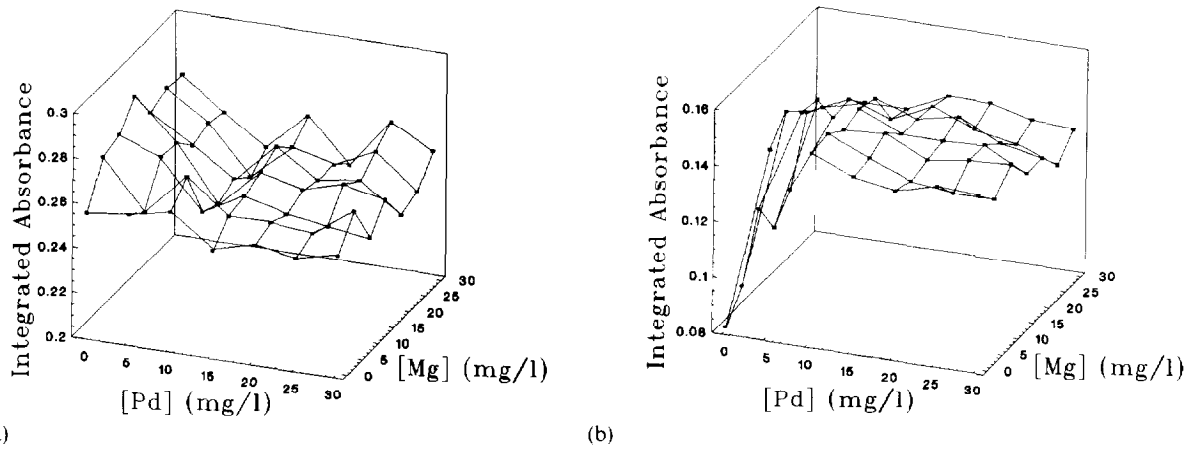

Fig. 2. Dependence of the chromium absorbance signal on the combined effects of various amounts of palladium and magnesium nitrate added to (a) cocaine sample solution spiked with 10 $\mu g\ l^{-1}$ of Cr^{3+} and (b) aqueous standard solution of 15 $\mu g\ l^{-1}$ of Cr^{3+}.

3.2. Optimization of the amount of chemical modifier

In order to investigate the use of magnesium nitrate, palladium–magnesium nitrate and palladium as chemical modifiers, and to determine their optimum amounts, a study involving different combinations of palladium and magnesium was performed. The charring temperature used was the optimum found for palladium–magnesium nitrate, 1500 °C, and the atomization temperature was 2500 °C. These experiments were carried out on cocaine sample solutions spiked with 10 $\mu g\ l^{-1}$ of Cr^{3+}, Fig. 2(a), and Cr^{3+} aqueous standard solutions of 15 $\mu g\ l^{-1}$, Fig. 2(b). The addition of palladium does not have any influence, as shown in Fig. 2(a). However, chromium absorbance values increase slightly, in the absence of palladium, until a concentration of 15 mg l^{-1} of magnesium nitrate is reached. These facts can also be observed in Figs. 3 and 4, where different peak schemes, corresponding to 0 mg l^{-1} of palladium and various amounts of magnesium, and 15 mg l^{-1} of magnesium and different amounts of palladium, respectively, are represented. In Fig. 2(b), which shows the results obtained for aqueous standards of Cr^{3+}, it can be seen that the addition of palladium increases the chromium absorbance signal. However, it should be mentioned that the higher chromium absorbance signals correspond to combinations between $Mg(NO_3)_2$ and Pd, where the amount of magnesium nitrate is greater than that of Pd. Therefore, the highest chromium absorbance is obtained for concentrations of 10 and 15 mg l^{-1} for palladium and magnesium nitrate, respectively. Because the addition of palladium to cocaine sample solutions does not offer a significant increase in chromium absorbance, we select magnesium alone, at a concentration of 15 mg l^{-1}, as adequate for stabilizing chromium.

The amount of nitric acid was optimized in the same way, increasing the concentration up to 10% (v/v) for aqueous standard solutions of 15 $\mu g\ l^{-1}$

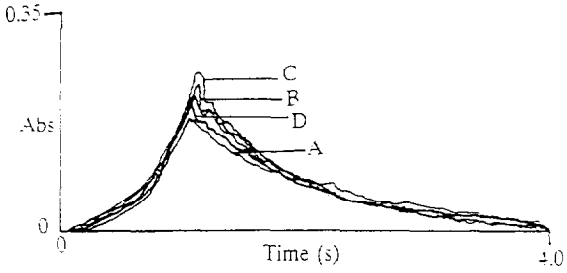

Fig. 3. Effect of 0 mg l^{-1} of palladium and different amounts of magnesium nitrate on the peak scheme corresponding to a cocaine sample solution spiked with 10 $\mu g\ l^{-1}$ of Cr^{3+}: (A) 0 mg l^{-1} (0.254 A.s.); (B) 5 mg l^{-1} (0.272 A.s.); (C) 15 mg l^{-1} (0.285 A.s.); (D) 25 mg l^{-1} (0.272 A.s.).

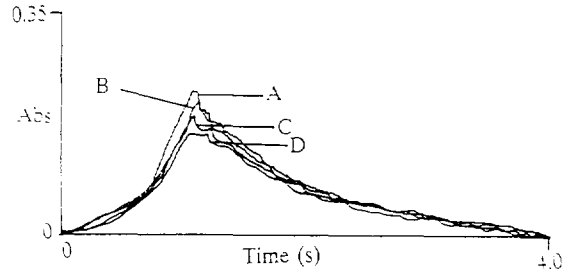

Fig. 4. Effect of 15 mg l^{-1} of magnesium nitrate and different amounts of palladium on the peak scheme corresponding to a cocaine sample solution spiked with 10 μg l^{-1} of Cr^{3+}: (A) 0 mg l^{-1} (0.285 A.s.); (B) 5 mg l^{-1} (0.267 A.s.); (C) 10 mg l^{-1} (0.243 A.s.); (D) 20 mg l^{-1} (0.246 A.s.).

of Cr^{3+} and a cocaine sample solution spiked with 10 μg l^{-1} of Cr^{3+}. Chromium absorbance was not statistically varied in the range studied and no variation in the peak scheme was found with larger amounts of nitric acid for both cocaine and aqueous solutions. Therefore, because an increase in the concentration of nitric acid results in faster damage of graphite tubes, we selected an optimum concentration of nitric acid of 3.5% (v/v), i.e. the concentration obtained after dissolution and dilution of cocaine samples in the autosampler cups (Section 2.3).

3.3. Optimization of the graphite furnace temperature programmes

Although chromium absorbance is stronger when magnesium nitrate is used instead of nitric acid, a temperature programme for nitric acid has also been developed and compared in terms of sensitivity, precision and accuracy to that for magnesium nitrate. The use of nitric acid as a chemical modifier is simpler than the use of magnesium nitrate because the optimum concentration of nitric acid, 3.5% (v/v), is that obtained after dissolution and dilution of cocaine in the autosampler cups; thus, it is only necessary to dilute the cocaine samples, without the addition of other species.

As mentioned previously, in the cases of nitric acid and magnesium nitrate a charring temperature of 1600°C was found to be optimal. Optimum values of the ramp and hold times for the charring step, corresponding to the use of magnesium nitrate and nitric acid, are shown in Table 1.

In order optimize the atomization temperatures for each chemical modifier, a range of temperatures between 1800 and 2600°C was studied for a cocaine sample solution spiked with 10 μg l^{-1} of Cr^{3+} and an aqueous solution of 15 μg l^{-1} of Cr^{3+}; these were the optimum temperatures for each chemical modifier and solution shown in Table 2.

Optimum drying conditions, temperatures and times, for each chemical modifier, were determinated by observing the sample in the graphite tube. In order to provide smooth evaporation of the solvent with no sputtering of the sample, an optimum temperature of 150°C with ramp and hold times of 15 s was achieved for both chemical modifiers.

3.4. Linear range, and calibration and standard addition graphs

The linear range was established for the use of magnesium nitrate and nitric acid, being 0.15–15 and 0.18–15 μg l^{-1} of Cr^{3+}, respectively. In order to determine the matrix effects for both methods, the standard addition method was applied over the same range of concentrations. The equations obtained for the use of magnesium nitrate were

calibration graph:

$$Q_A = 0.008 + 0.017[Cr^{3+}] \quad r = 0.999$$

standard addition graph:

$$Q_A = 0.049 + 0.020[Cr^{3-}] \quad r = 0.999$$

Table 2
Optimum atomization temperatures corresponding to different chemical modifiers

Chemical modifier	Atomization temperature (°C)	
	Cocaine sample solution	Aqueous Cr standard
Palladium	2600	2600
Palladium–magnesium nitrate	2600	2600
Magnesium nitrate	2500	2600
Nitric acid	2500	2600

Table 3
Analytical recovery ($n = 11$) corresponding to the use of magnesium nitrate and nitric acid as chemical modifiers

Cr^{3+} concentration added ($\mu g\ l^{-1}$)	$Mg(NO_3)_2$			HNO_3		
	Cr^{3+} concentration found ($\mu g\ l^{-1}$)	Analytical recovery (%)	RSD (%)	Cr^{3+} concentration found ($\mu g\ l^{-1}$)	Analytical recovery (%)	RSD (%)
5.0	4.87 ± 0.07	96.4 ± 1.4	2.3	5.23 ± 0.09	$104.5 \pm 2{,}0$	2.8
7.5	7.32 ± 0.09	97.6 ± 1.2	1.8	7.53 ± 0.05	100.4 ± 0.7	1.0
10.0	10.3 ± 1.2	103.5 ± 1.2	1.7	9.88 ± 0.09	98.8 ± 0.9	1.4

and for the use of nitric acid were

calibration graph:

$$Q_A = 0.011 + 0.017[Cr^{3+}] \quad r = 0.997$$

standard addition graph:

$$Q_A = 0.041 + 0.014[Cr^{3+}] \quad r = 0.999$$

where Q_A is the integrated absorbance and $[Cr^{3+}]$ is in units of $\mu g\ l^{-1}$.

The F-test [32] was applied to comparison of the slopes in each graph and for each chemical modifier; in both cases, the slopes of the calibration and standard addition graphs were statistically the same, and thus there are no matrix effects in the determination of chromium when using magnesium nitrate or nitric acid. Aqueous calibration was found to be a real possibility for developing the analysis for the use of both chemical modifiers.

3.5. Sensitivity

The sensitivity of magnesium nitrate and nitric acid as chemical modifiers was studied for the two programmes (Table 1). The limit of detection (LOD), limit of quantification (LOQ) and characteristic mass (m_0) [33] were the parameters used in the study.

The blanks were solutions of 3.5% (v/v) nitric acid when using nitric acid as a chemical modifier, and 3.5% (v/v) of nitric acid and 15 mg l^{-1} of magnesium nitrate when using magnesium nitrate as a modifier. The values obtained, for 11 replicate injections, were 0.008 ± 0.001 and 0.006 ± 0.001 A.s. for magnesium nitrate and nitric acid, respectively.

The LODs, corresponding to 0.5 g of drug sample, were 5.77 and 7.23 μg^{-1} for the use of magnesium nitrate and nitric acid, respectively, the LOQs being 19.24 $\mu g\ kg^{-1}$ for magnesium nitrate and 24.20 $\mu g\ kg^{-1}$ for nitric acid. The values of m_0 obtained were 5.2 ± 0.34 and 4.6 ± 0.67 pg for magnesium nitrate and nitric acid, respectively. As can be seen, the sensitivity is better for magnesium nitrate as a chemical modifier.

3.6. Precision and accuracy

Precision was studied for the use of both chemical modifiers, magnesium nitrate and nitric acid. The within-batch precisions obtained for 11 replicate injections of cocaine sample solutions spiked with 0, 5, 7.5 and 10 $\mu g\ l^{-1}$ of Cr^{3+}, expressed as RSDs, were 7.45, 2.21 0.86 and 1.19%, respectively, for nitric acid, and 6.19, 1.78, 1.52 and 1.48%, respectively, for magnesium nitrate. As can be seen, similar precision is achieved by both chemical modifiers.

The accuracy of the methods was studied by analytical recovery. This parameter was obtained for cocaine solutions spiked with 5, 7.5 and 10 $\mu g\ l^{-1}$ of Cr^{3+}, which were injected into the atomizer 11 times. The results are shown in Table 3. As can be seen, analytical recoveries close to 100% were achieved for all concentration levels for both chemical modifiers.

Good precision and analytical recovery were discovered for both the chemical modifiers investigated, and a similar linear range was achieved. Therefore, owing to the lower LOD obtained with the use of magnesium nitrate, we consider magnesium nitrate to be a more suitable chemical

modifier than nitric acid. In the following studies, magnesium nitrate, at the optimum concentration of 15 mg l^{-1}, will be used.

3.7. Study of the introduction of a cooling-down step

The introduction of a cooling-down step, which has been reported for the determination of lead and aluminiun [34], has also been implemented in the determination of chromium in foodstuffs [24]. Therefore, in this section a graphite furnace temperature programme incorporating a cooling-down step, just before atomization, with ramp and hold times of 10 s for each and cooling temperatures between 50 and 350°C, was studied. The within-run precision, for seven replicate injections of a cocaine sample solution spiked with 10 μg l^{-1} of Cr^{3+}, was studied for each cooling temperature, obtaining good precision ($< 10\%$) for measurements in the peak-area and peak-height modes. However, the RSD (%) values for higher cooling temperatures were larger than those for lower cooling temperatures and those similar to the values obtained without the introduction of a cooling-down step (Table 1). An increase in chromium absorbance, measured in the peak-area mode, compared to that obtained using the former programme, was obtained for all cooling temperatures.

A cooling temperature of 50°C was selected as the most adequate cooling temperature owing to good within-run precision and the peak scheme attained. However, the sensitivity achieved was poorer than that obtained using the former programme (Table 1), the LOD being three times higher (19.24 μg kg^{-1}) than the standard programme (5.77 μg kg^{-1}).

3.8. Interferences

A study on the effects of species that could interfere with the chromium absorbance signal was carried out. We assume a species to be an interferent when, at a specified concentration, it produces a variation in the chromium absorbance signal of $\pm 10\%$ of the signal measured in the absence of the species. Therefore, several different cations, Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, K^+, Li^+, Mn^{2+}, Na^+, NH_4^+, Ni^{2+}, Pb^{2+} and Zn^{2+}, and anions, Cl^-, PO_4^{3-}, SO_4^{2-}, SiO_3^{2-} and citrate, were studied. Different amounts of each species were added to a cocaine sample solution spiked with 10 μg l^{-1} of Cr^{3+}; the results obtained are shown in Table 4, which gives the lowest concentration corresponding to 0.5 g of the drug sample, the percentage chromium absorbance variation and the levels for some species reported in the literature [1]. As can be seen, species that can be considered as major constituents, such as Ca^{2+}, Mg^{2+} and Zn^{2+}, do not exhibit interfering behaviour. Similarly, for anions such as Cl^-, PO_4^{3-} and SO_4^{2-}, that could also be considered as major constituents, the addition of 100 mg l^{-1} (4000 mg kg^{-1} corresponding to sample) does not statistically vary the ab-

Table 4
Effects of different elements on the chromium absorbance signal of a cocaine sample solution spiced with 10 μg l^{-1} of Cr^{3+}

Interferent	Lowest concentration with respect to sample (mg kg^{-1})	Concentration interval (mg kg^{-1})	% Chromium absorbance variation
Al^{3+}	2000	0.5–2700	+10.2
Ba^{2+}	120	0.1–26	−3.6
Ca^{2+}	4000	–[a]	+5.1
Cd^{2+}	120	0.1–2.1	−1.6
Co^{2+}	120	–[a]	−1.1
Cu^{2+}	400	0.7–270	−6.4
Fe^{3+}	4000	2.7–2200	+14.7
K^+	4000	–[a]	+3.0
Li^+	1200	–[a]	+7.5
Mg^{2+}	4000	–[a]	+3.4
Mn^{2+}	1200	0.5–220	−0.5
Na^+	4000	–[a]	−7.5
NH_4^+	1200	–[a]	−0.5
Ni^{2+}	80	0.0–77	−4.8
Pb^{2+}	80	0.3–2.1	−0.5
Zn^{2+}	4000	0.1–2600	−0.4
Citrate	4000	–[a]	−1.1
Cl^-	4000	–[a]	−2.2
PO_4^{3-}	4000	–[a]	−0.5
SiO_3^{2-}	1200	–[a]	+4.3
SO_4^{2-}	4000	–[a]	−6.6

[a] Data not available.

sorbance signal. Interfering behaviour is only obtained at concentrations of Fe^{3+} and Al^{3+} greater than 2000 mg kg^{-1}. Although this fact has been observed by several authors [7,8,35,36], no explanation has been reported. Finally, for the other species whose concentration levels are available, there are no observed interfering effects at the highest concentration tested, which is greater than that reported in these kinds of samples.

3.9. Study of precision and analytical recovery with the amount of sample

A study on the precision and analytical recovery for different amounts of drug samples was developed in order to reduce the LOD and LOQ, and to verify if the amount of drug sample chosen, 0.5 g, is a representative mass to carry out the analysis. Therefore, 0.25, 0.5, 1.0 and 2.0 g cocaine samples were prepared as indicated in Section 2.3, obtaining sample concentrations of 2.5, 5.0, 10.0 and 20.0% (m/v), respectively, after dilution to 10 ml. The volume of nitric acid used to dissolve the samples was 2 ml (Section 2.3); however, for an amount of sample of 2 g, it was necessary to increase the volume of nitric acid to 2.5 ml to totally dissolve the sample.

The effect of the different sample concentration precisions was studied through the within-run precision, for 11 replicate injections of the solutions prepared from each amount of sample. To obtain similar chromium absorbance values, different volumes of an aqueous standard solution of Cr^{3+} were added to the solutions of lower sample concentrations. The RSD values obtained were 2.03, 0.72, 1.38 and 1.36% for 2.5, 5.0, 10.0 and 20.0% (m/v), respectively. As can be seen, the increase in the amount of sample does not impair the precision.

To study the effect of the amount of sample on the analytical recovery, each cocaine sample solution, corresponding to each amount of sample, spiked with 5 and 10 $\mu g\ l^{-1}$ of Cr^{3+}, was injected 11 times into the graphite furnace, and the analytical recoveries were determined. The results are shown in Table 5, where it can be seen that for all sample concentrations and for the two concentration levels tested, analytical recoveries closed to 100% were achieved.

Table 5
Analytical recovery ($n = 11$) corresponding to different sample concentrations

Sample concentration (% (w/v))	Analytical recovery (%)	
	+5 $\mu g\ l^{-1}$ Cr^{3+}	+10 $\mu g\ l^{-1}$ Cr^{3+}
2.5	102.4 ± 1.0	99.6 ± 0.9
5.0	97.4 ± 1.4	103.5 ± 1.2
10.0	96.6 ± 2.6	101.6 ± 1.6
20.0	92.8 ± 3.6	102.0 ± 1.9

Therefore, the amount of sample can be increased to 2 g of drug sample without a loss of analytical performance, attaining a LOD of 1.44 $\mu g\ kg^{-1}$.

However, 0.5 g of drug sample can be considered as an adequate and representative mass for developing the analysis due to precision, and analytical recovery is not statistically varied in the 0.25–2.00 g range, obtaining an adequate LOD for the determination of chromium in a great number of samples.

3.10. Application

The method, using magnesium nitrate as a chemical modifier, was applied to the determination of chromium content in cocaine and heroin samples from various geographical areas. One subsample was taken from each sample and prepared as in Section 2.3, and two subsamples from each were subjected to FAAS twice. The results obtained are shown in Table 6, together with the SDs for four analyses of each drug sample. The obtained concentrations of chromium are low, those in heroin (0.05–0.59 mg kg^{-1}) being slightly bigger than those in cocaine (0.02–0.14 mg kg^{-1}). This can be attributed to the lower purity of the heroin samples compared to the cocaine samples. It can be said that the chromium levels found for cocaine and for some heroin samples are lower than 0.2 mg kg^{-1}, which is the lowest concentration of chromium reported by Violante et al. [1].

Table 6
Chromium levels found in several heroin and cocaine samples

Sample		Chromium level (mg kg^{-1})	SD[a] (mg kg^{-1})
Heroin	1	0.33	0.05
	2	0.15	0.10
	3	0.05	0.04
	4	0.32	0.12
	5	0.59	0.08
Cocaine	1	0.14	0.05
	2	0.07	0.03
	3	0.09	0.06
	4	0.06	0.04
	5	0.07	0.04
	6	0.08	0.04
	7	0.06	0.04
	8	0.13	0.06
	9	0.06	0.05
	10	0.06	0.05
	11	0.06	0.03
	12	0.02	0.03

[a] $n = 4$.

4. Conclusions

The results of this work confirm the advantageous application of magnesium nitrate as a chemical modifier for the determination of chromium. With the use of this chemical modifier, matrix effects are satisfactorily removed and aqueous calibration is a real possibility. In addition, magnesium nitrate offers the lowest LOD and LOQ, thus giving acceptable precision and accuracy. Finally, it should be mentioned that the introduction of a cooling-down step before atomization, recommended by several authors for chromium determination [24], does not offer any advantage in terms of sensitivity.

References

[1] N. Violante, M.G. Quaglia, A. Lopez and S. Caroli, Microchem. J., 45 (1992) 79.
[2] B. Welz, Atomic Absorption Spectrometry, 2nd edn., VCH, Weinheim, 1985, p. 279.
[3] Y.Q. Zhang, D.J. Wang, J.C. Cui, L.M. Zhang, Y.L. Ren and Y.S. Zheng, Guangpuxue Yu Guangpu Fenxi, 12 (1992) 71.
[4] H. Minami, Q. Zhang, H. Itoh and I. Atsuya, Microchem. J., 49 (1994) 126.
[5] V.A. Granadillo, L. Parra de Machado and R.A. Romero, Anal. Chem., 66 (1994) 3624.
[6] D.C. Paschal and G.G. Bailey, At. Spectrosc., 12 (1991) 151.
[7] E. Beceiro-González, J. Barciela-García, P. Bermejo-Barrera and A. Bermejo-Barrera, Fresenius' J. Anal. Chem., 344 (1992) 301.
[8] E. Beceiro-González, P. Bermejo-Barrera, A. Bermejo-Barrera, J. Barciela-García and C. Barciela-Alonso, J. Anal. At. Spectrom., 8 (1993) 649.
[9] S.C. Apte, S.D.W. Comber, M.J. Gardner and A.M. Gunn, J. Anal. At. Spectrom., 6 (1991) 169.
[10] K. Pyrzynska, Anal. Lett., 22 (1989) 2847.
[11] S. Chen, S. Lin, G. Zhou, W. Qi and Y. Qian, Fenxi Huaxue, 18 (1990) 645.
[12] S. Xiao-Quan, Z. Yan and N. Zhe-Ming, At. Spectrosc., 11 (1990) 116.
[13] G. Tan, M. Liu and Lihua Jianyan, Huaxue Fence, 27 (1991) 7.
[14] R. Liu, D. Yan and Z. Zheng, Fenxi Shiyanshi, 11 (1992) 43.
[15] J.L. Manzoori and A. Saleemi, J. Anal. At. Spectrom., 9 (1994) 337.
[16] Y.Z. Ma, B.W. Li, Z.K. Li, J.Z. Wang and Y.Q. Li, Fenxi Huaxue, 21 (1993) 745.
[17] R.F.J. Stobbaerts and H.A. Deelstra, Bull. Soc. Chim. Belg., 98 (1989) 513.
[18] U. Völlkopf, Z. Grobenski and B. Welz, At. Spectrosc., 4 (1983) 165.
[19] Z. Grobenski, R. Lehmann, B. Radziuk and U. Völlkopf, At. Spectrosc., 5 (1984) 87.
[20] W. Slavin and G.R. Carnrick, At. Spectrosc., 6 (1985) 157.
[21] K.S. Subramanian, Prog. Anal. Spectrosc., 9 (1986) 237.
[22] F. Betts and A. Yau, Anal. Chem., 61 (1989) 1235.
[23] D. Wagley, G. Schmiedel, E. Mainka and H.J. Ache, At. Spectrosc., 10 (1989) 106.
[24] N.J. Miller-Ihli and F.E. Greene, J. Assoc. Off. Anal. Chem., 75 (1992) 354.
[25] S. Cuo, C. Wang and G. Sheng, Fenxi Huaxue, 17 (1989) 937.
[26] G. Benling and L. Yongming, At. Spectrosc., 11 (1990) 229.
[27] E. Álvarez-Cabal Cimadevilla, K. Wróbel, J.M. Marchante-Gayón and A. Sanz-Medel, J. Anal. At. Spectrom., 9 (1994) 117.
[28] M. Hoeing, P. Regnier and R. Wollast, At. Spectrosc., 5 (1984) 87.
[29] R.C. Weast, CRC Handbook of Chemistry and Physics, 65th edn., CRC Press, Boca Raton, FL, 1984, p. B-88.
[30] G. Schlemmer and B. Welz, Spectrochim. Acta, Part B, 41 (1986) 1157.
[31] B. Welz, G. Schlemmer and R.G. Mudakavi, J. Anal. At. Spectrom., 3 (1988) 695.

[32] J.C. Miller and J.N. Miller, Statistics for Analytical Chemistry, 2nd edn., Wiley, New York, 1986, p. 57.
[33] L.H. Keith, W. Crummett, J. Deegan, R.A. Libby, J.K. Taylor and G. Wenther, Anal. Chem., 55 (1983) 2210.
[34] M.W. Hinds, M. Katyal and K.W. Jackson, J. Anal. At. Spectrom., 3 (1988) 83.
[35] K. Matsusaki, T. Yoshino and Y. Yamamoto, Anal. Chim. Acta, 124 (1981) 163.
[36] D.C. Manning, W. Slavin and G.R. Carnrick, Spectrochim. Acta, Part B, 37 (1982) 331.